

Size Induced Shifts in the Thermodynamics of Nanophase Oxides and Implications for Materials Science, Geochemistry, and Environmental Science

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Energy, Environment, Resources, Climate

- Mineralogical, solid state chemical and thermodynamic aspects of
 - CO₂ management
 - Nuclear energy
 - Water
 - Metals
 - **No free lunch**
 - **Science – policy – politics**
 - **Thermodynamics wins in the long run**

Main Issue

- Synthetic and natural nanomaterials are often forced, by low temperature aqueous conditions, to remain fine grained, with particle sizes of 1-100 nm.
- How does this constraint alter thermodynamics, phase equilibria, and the occurrence of specific crystal structures?
- Different phases have different surface energies, thus their stability is affected differently by grain size diminution
- OXIDES AND OXYHYDROXIDES OF Ti, Mn, Fe, Co, Zn, Al, Zr, Hf, Ce, U.....

Magnitudes

- Effect on free energy of reaction:
 - Surface energies range from 0.5 to 5 J/m². Take Δ (surface energy) = 2 J/m²
 - Take surface area = 100 m²/g
 - Take molecular weight = 150 g/mol
 - $\Delta G = 2 \times 100 \times 150 \Rightarrow$ **30 kJ/mol**
 - General principle - small grain size *thermodynamically* stabilizes phase assemblage with lower surface energy

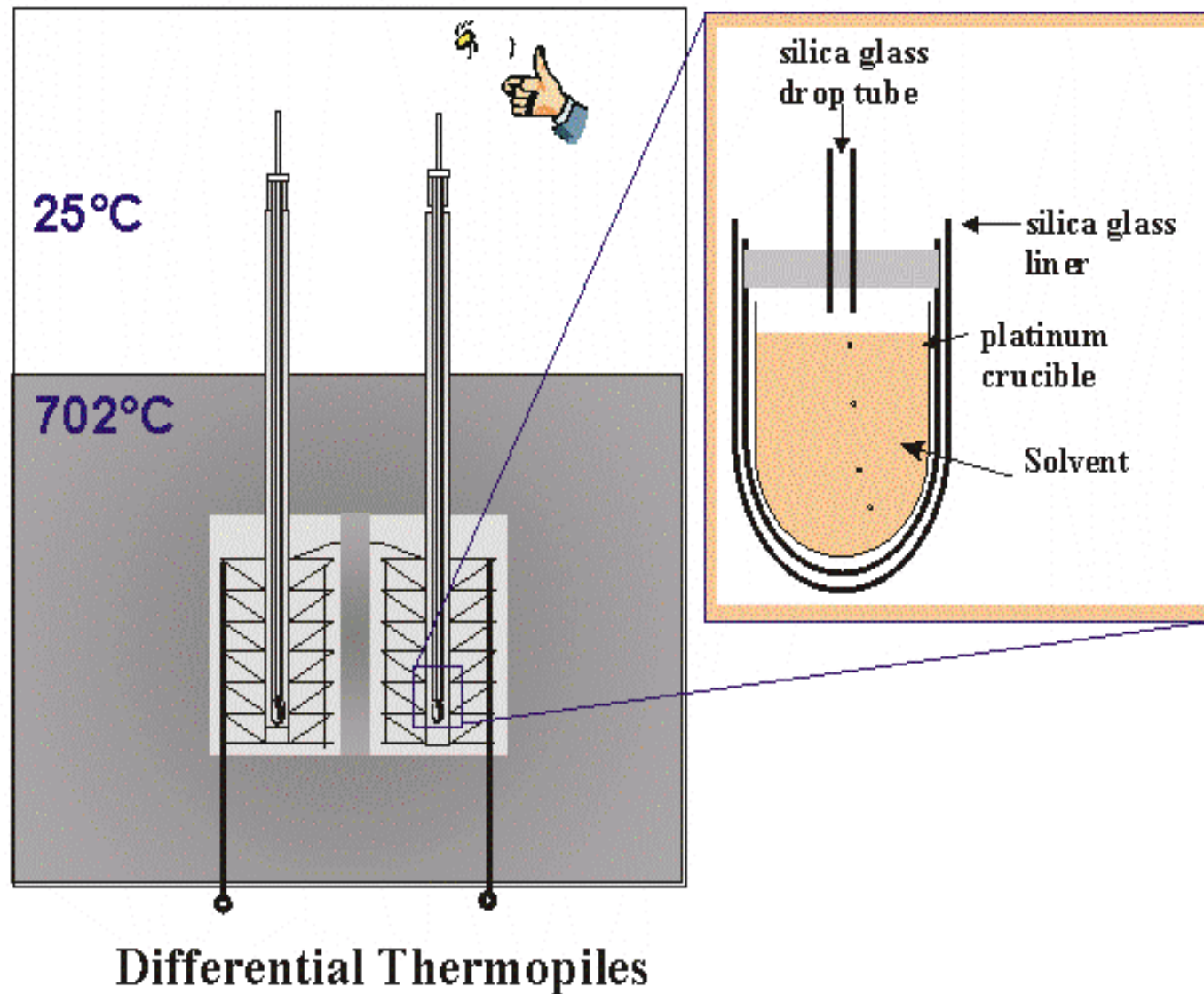
Calorimetric Measurement of Surface Enthalpies (Energies)

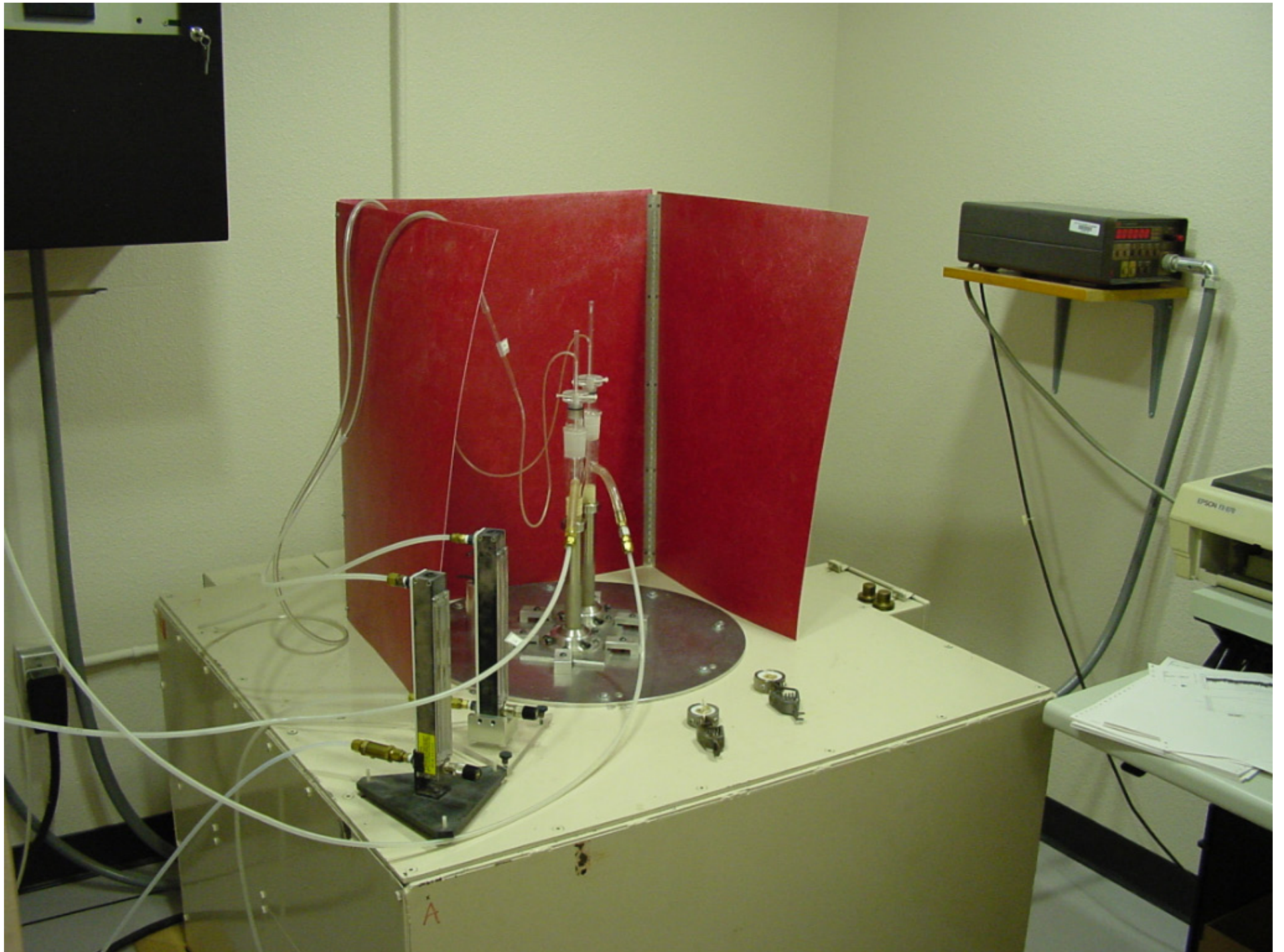
- Measure enthalpy of solution versus surface area, slope of line will give surface energy

Complications

- **Particles are hydrated and hold water strongly**
- **Particles may be agglomerated, twinned, etc. so sizes estimated by Xray, TEM, BET may differ and interfacial energies may play a role**

High temperature oxide melt drop-solution calorimetry

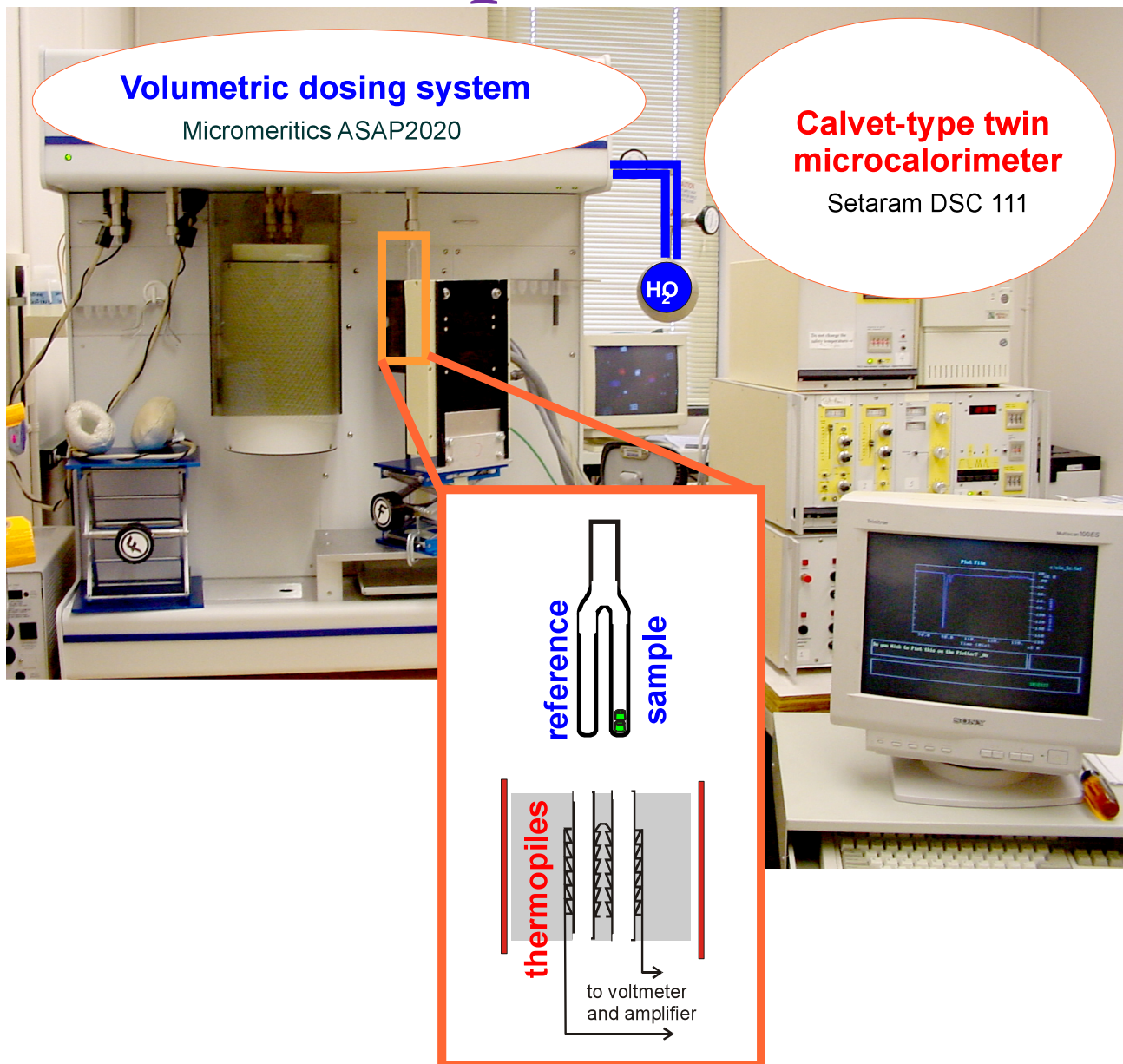


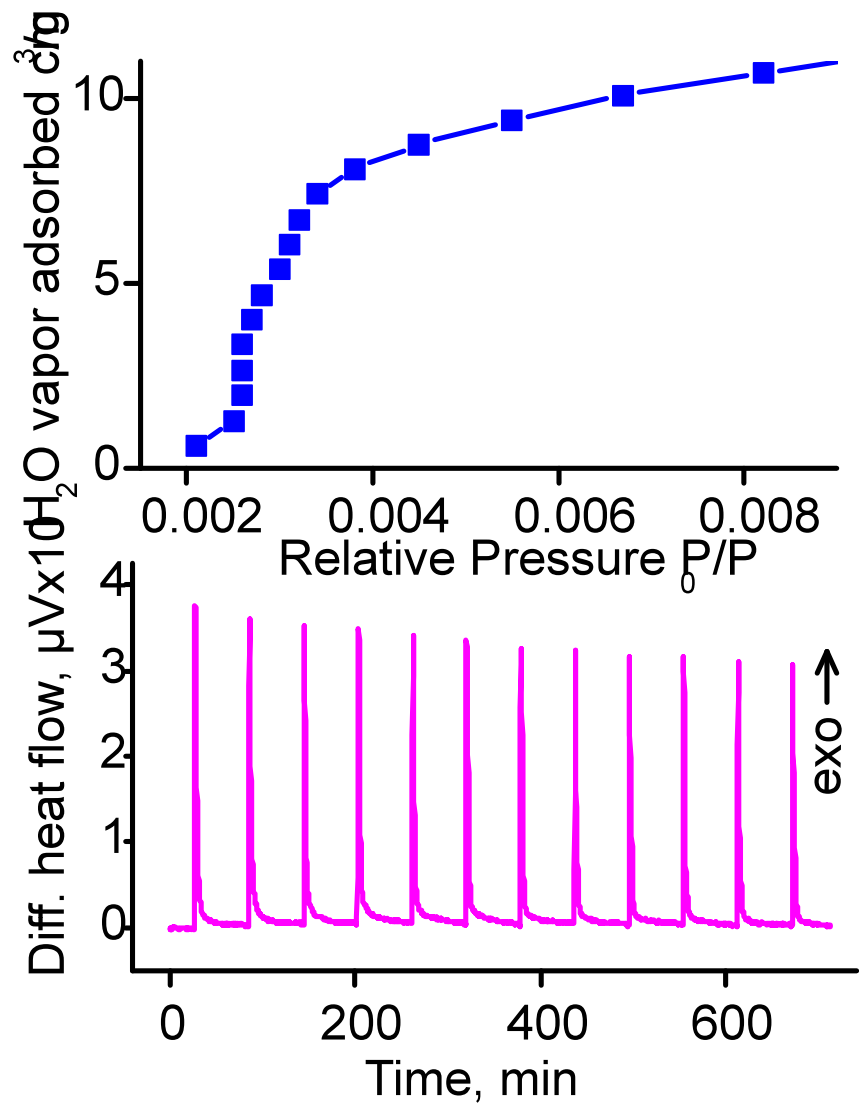


Commercial Setaram AlexSYS Calorimeter



Water Adsorption Calorimetry





H₂O Correction: Thermodynamic Cycle

One wants

(1) MO (nano, 298 K) → MO(dissolved, 973 K)

One measures

(2) MO·nH₂O (nano, 298 K) → MO(dissolved, 973 K) + nH₂O (gas, 973 K)

(3) H₂O (gas, 973 K) → H₂O (gas, 298 K)

(4) MO (nano, 298 K) + nH₂O (gas, 298 K) → MO·nH₂O (nano, 298 K)

(1) = (2) + n(3) + (4)

$\Delta H_1 = \Delta H_2 + n\Delta H_3 + \Delta H_4$

If ΔH_4 is heat of condensation of pure H₂O (-44 kJ/mol) then ΔH_1 refers to hydrated particle surfaces

If ΔH_4 is obtained from water adsorption enthalpy and is more negative than -44 kJ/mol, then ΔH_1 refers to anhydrous particle surfaces

Control of Polymorphism at the Nanoscale

- Competition between polymorphism and surface energy
- Free energy crossovers as function of size
- More metastable polymorphs have lower surface energies in general
- So nanoscale effects change what phase is stable when system is constrained not to coarsen : **STABILITY CROSSOVERS AT NANOSCALE**

Alumina

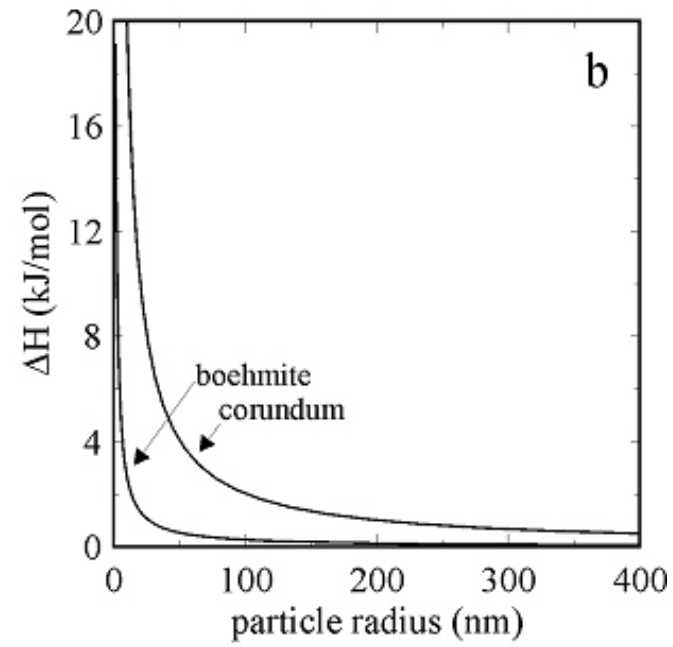
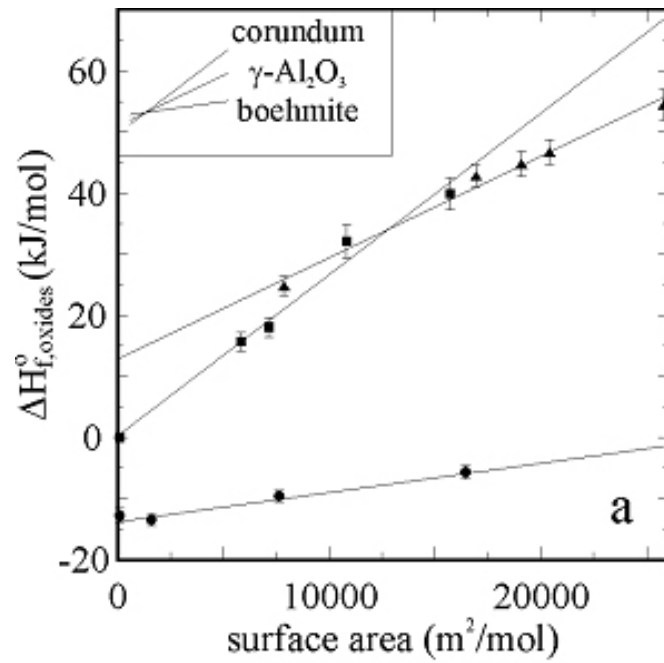
α - Al_2O_3 -corundum- the stable bulk phase based on hcp oxygen packing with Al in octahedral coordination

γ - Al_2O_3 - a defect spinel, ccp oxygens and Al and vacancies in both octahedral and tetrahedral coordination. Produced by low temperature dehydration of oxyhydroxides and hydroxides, generally high surface area and poor crystallinity

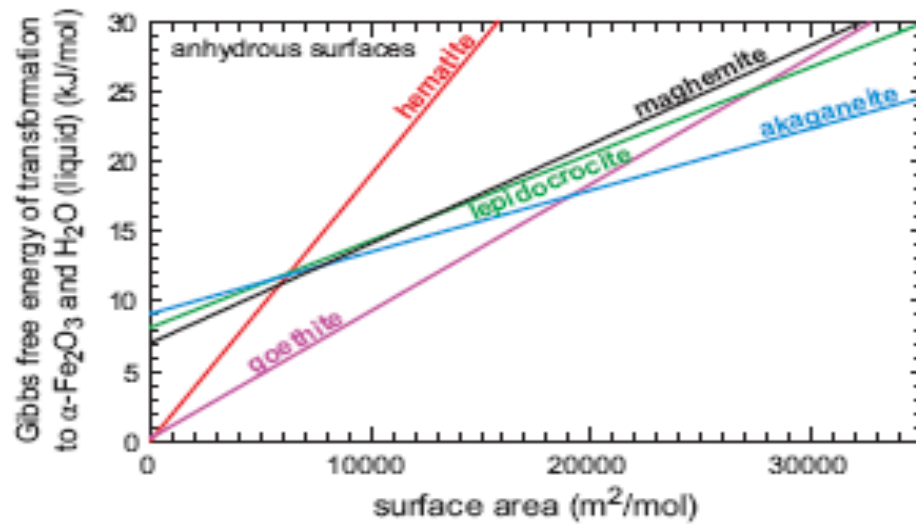
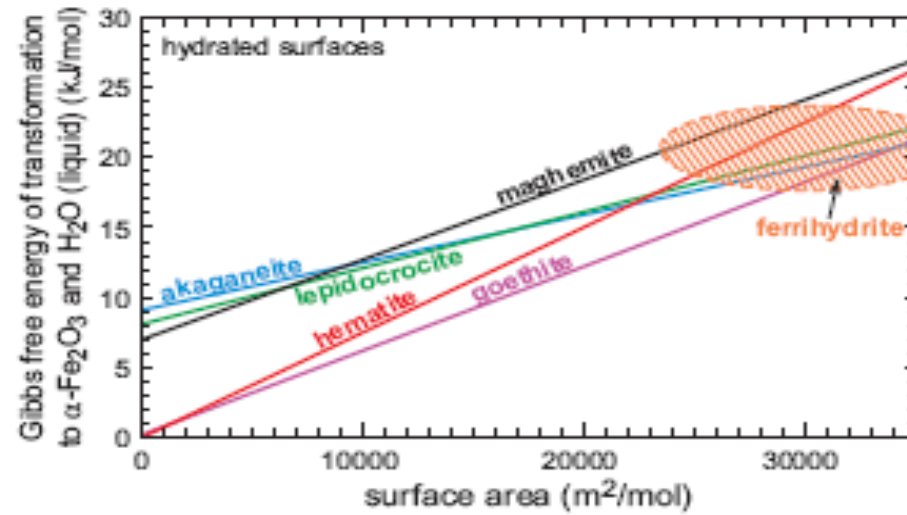
Different physical and catalytic properties.

Is γ - Al_2O_3 stabilized at the nanoscale by having lower surface energy than α ?

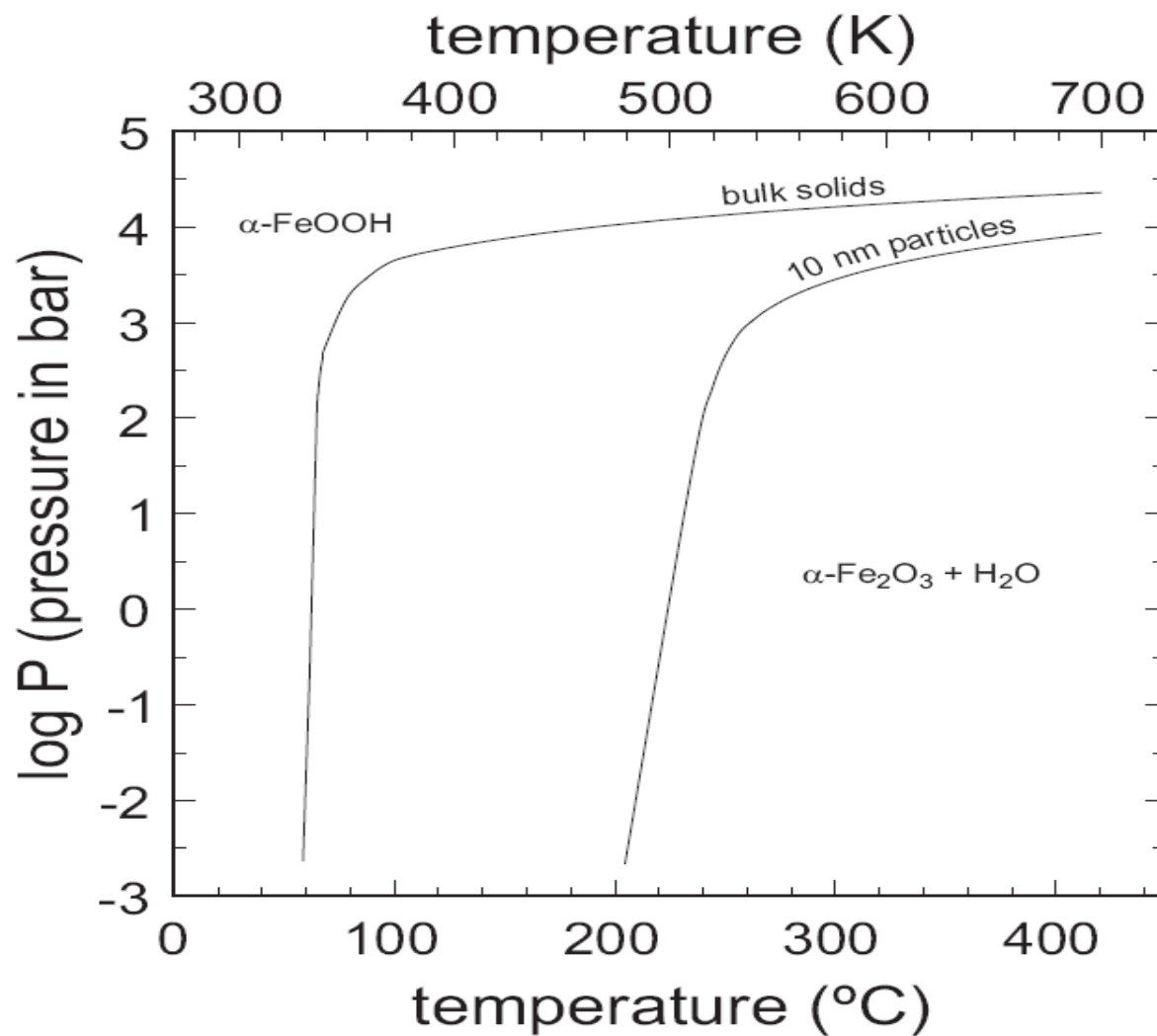
Alumina



Enthalpy of Iron Oxides Relative to Bulk Hematite plus Water



Goethite = Hematite + Water



Oxidation State Effects

- Obviously nanoparticles oxidize and reduce faster than bulk, and may be catalytically more active. But there are also thermodynamic effects
- Rocksalt oxides have higher surface energy than spinels. Oxides have higher surface energy than metals. Spinels have lower surface energies than trivalent non spinel oxides
- New data on CoO nanoparticles. They reduce water to hydrogen at room temperature, producing nano Co_3O_4 . They are reduced to Co metal under vacuum at room temperature. Hydration state also plays a role.
- Similarly Fe_3O_4 stability expands at the nanoscale.
- Mn oxides- surface energy increases in the order hausmannite, bixbyite, pyrolusite (coincidentally with increasing oxidation state)

Measured surface energies of spinels (J/m²) for anhydrous surface

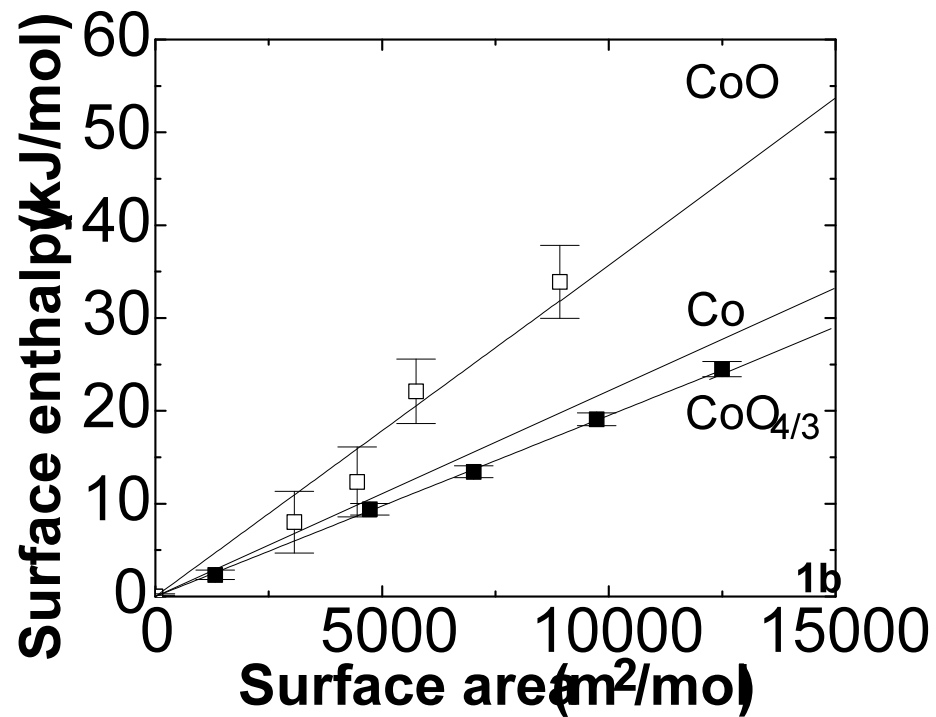
$\text{Al}_{8/3}\text{O}_4$	1.5
$\text{Fe}_{8/3}\text{O}_4$	0.7
MgAl_2O_4	1.8
Mn_3O_4	1.6
Fe_3O_4	1.4
Co_3O_4	2.0

Rocksalt divalent oxides and trivalent oxides have higher surface energies, typically in the 2-4 J/m² range

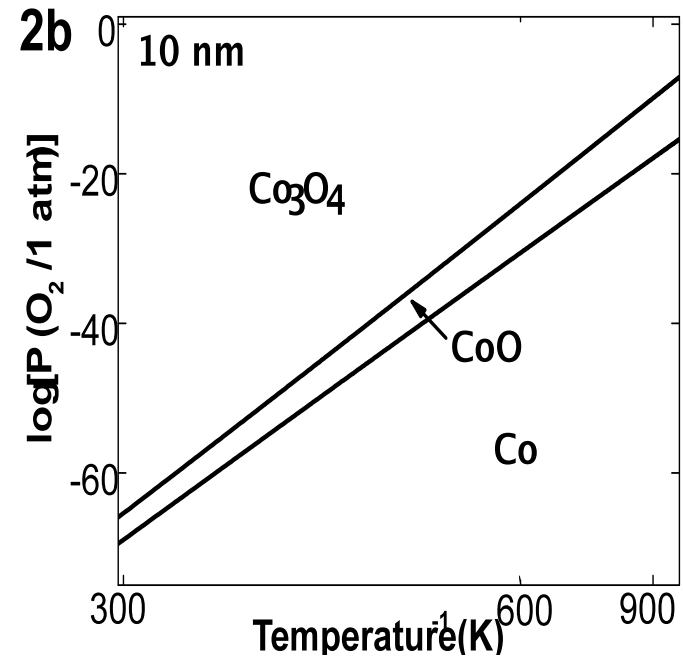
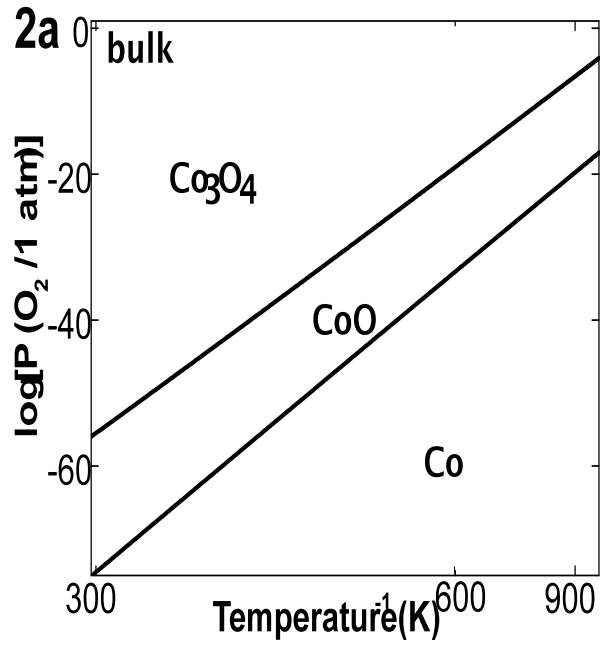
Surface Energy Systematics

- Spinel ($\gamma\text{-Al}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, MgAl_2O_4 , Co_3O_4 , Fe_3O_4 , Mn_3O_4 , Fe_2TiO_4) all have lower surface energies than divalent, trivalent, or tetravalent binary oxides.
- Olivines and perovskites have higher surface energies
- Layered materials have low surface energies
- **This appears general and is generally supported by DFT calculations**

Enthalpy relative to bulk phase as function of surface area in Co-O system

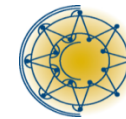
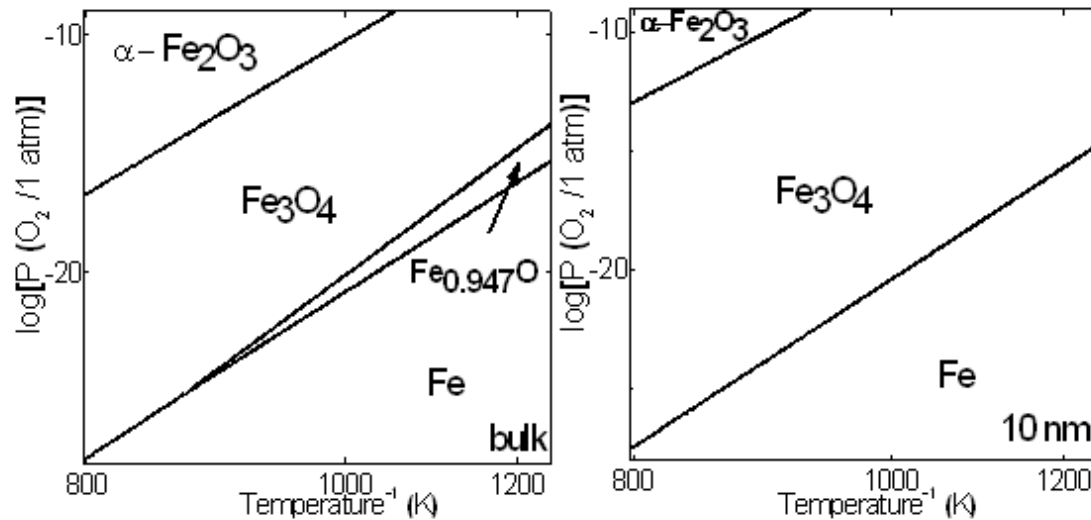


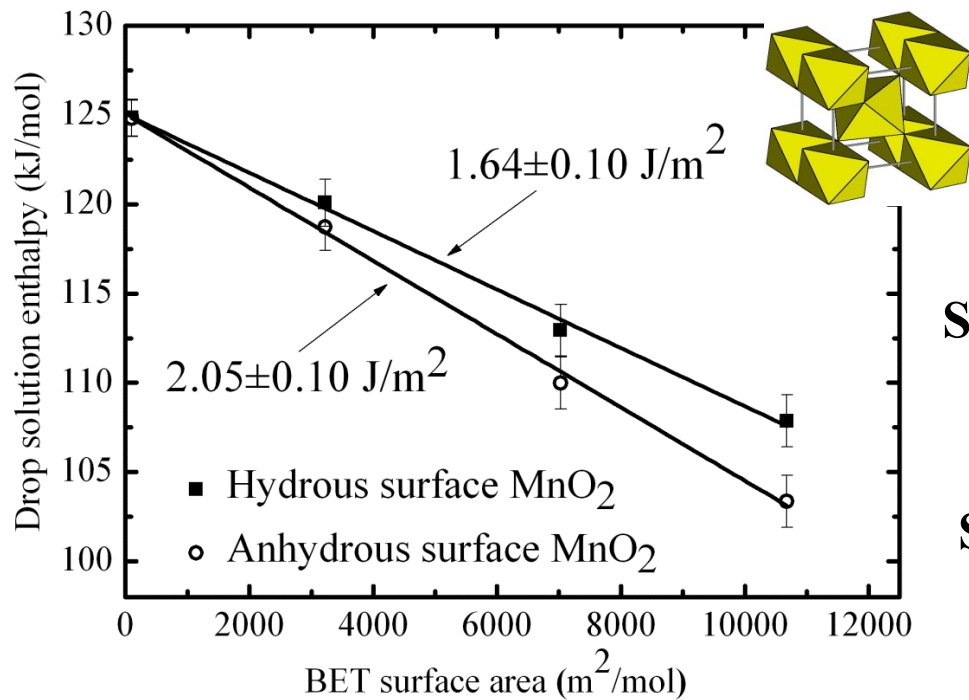
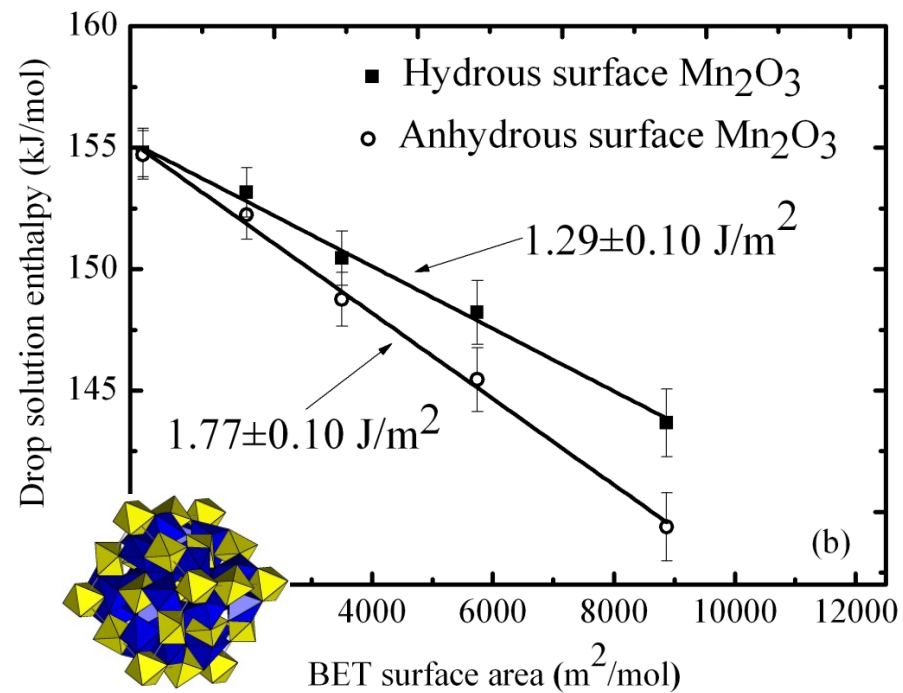
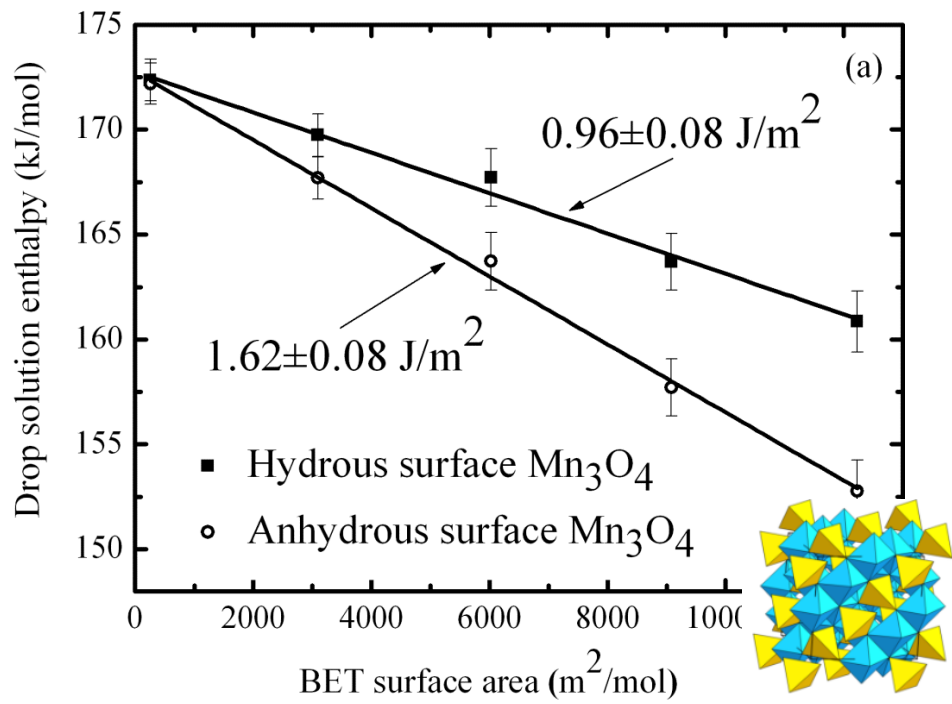
Co – O Phase Diagram



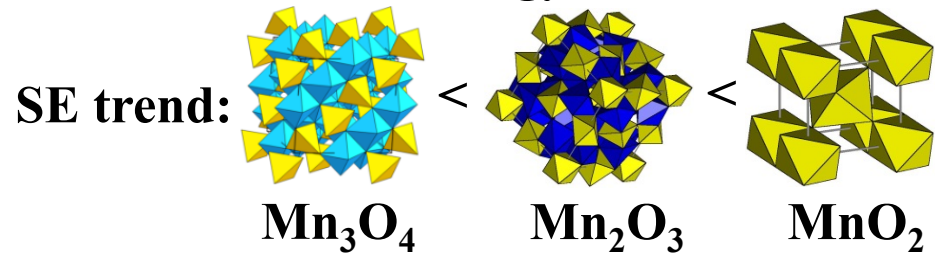
Oxidation-Reduction Equilibria among Transition Metal Oxides Change Dramatically at the Nanoscale Because of Differences in Surface Energies

- Relevant to materials processing, environmental science, geology, and even biology
- For example, for 10 nm iron oxides, wustite FeO has no stability field at all, with iron coexisting with magnetite
- Spinel, M_3O_4 have lower surface energies than divalent oxides MO and trivalent oxides M_2O_3 , expanding the spinel stability field.
- Navrotsky et al. Science 330, 199-201 (2010)



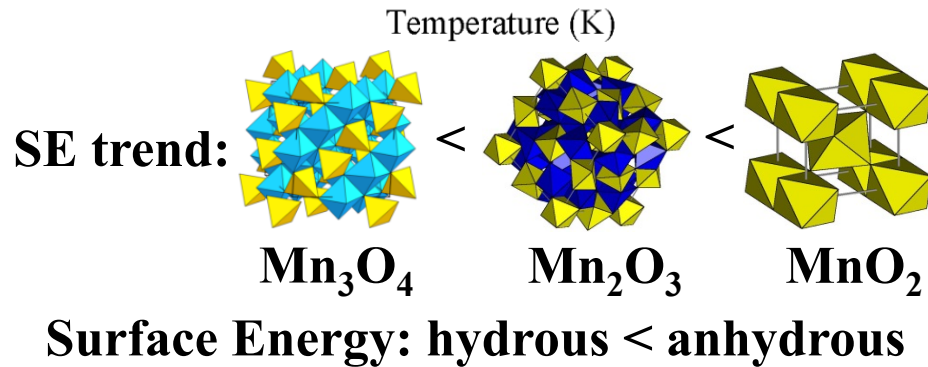
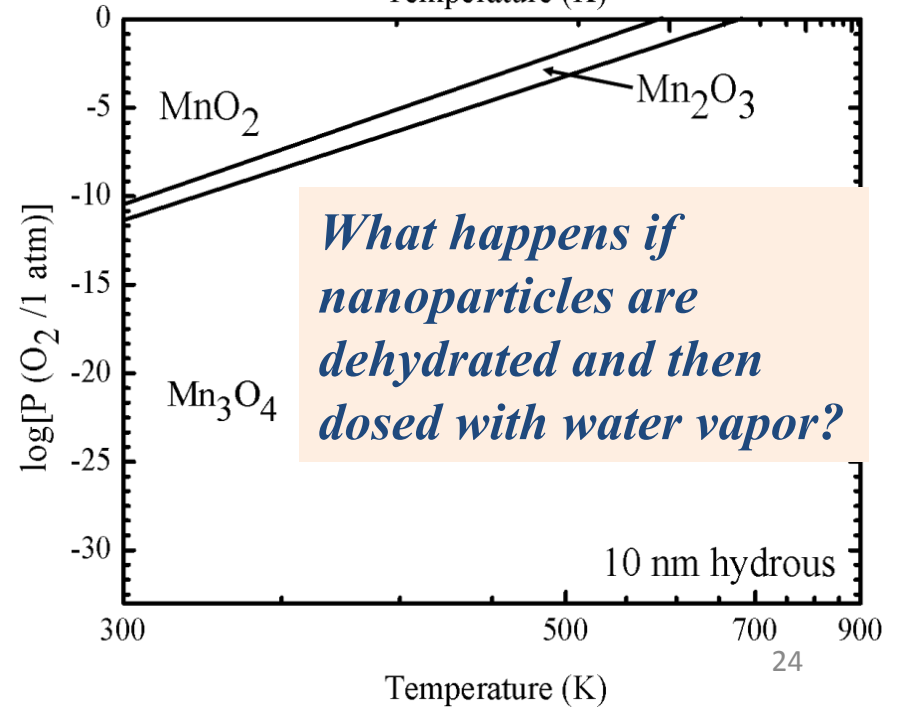
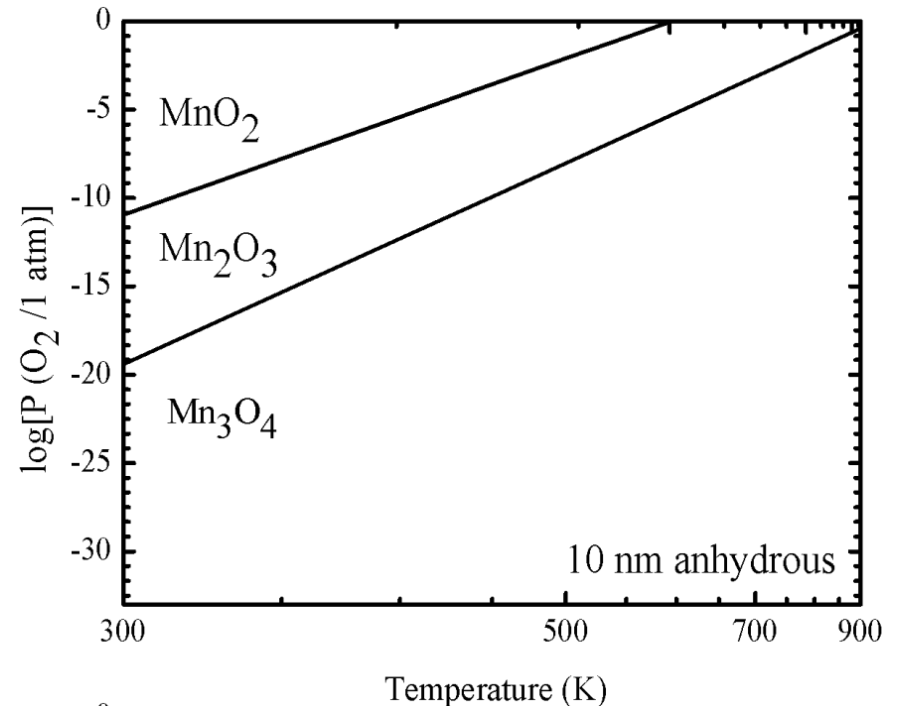
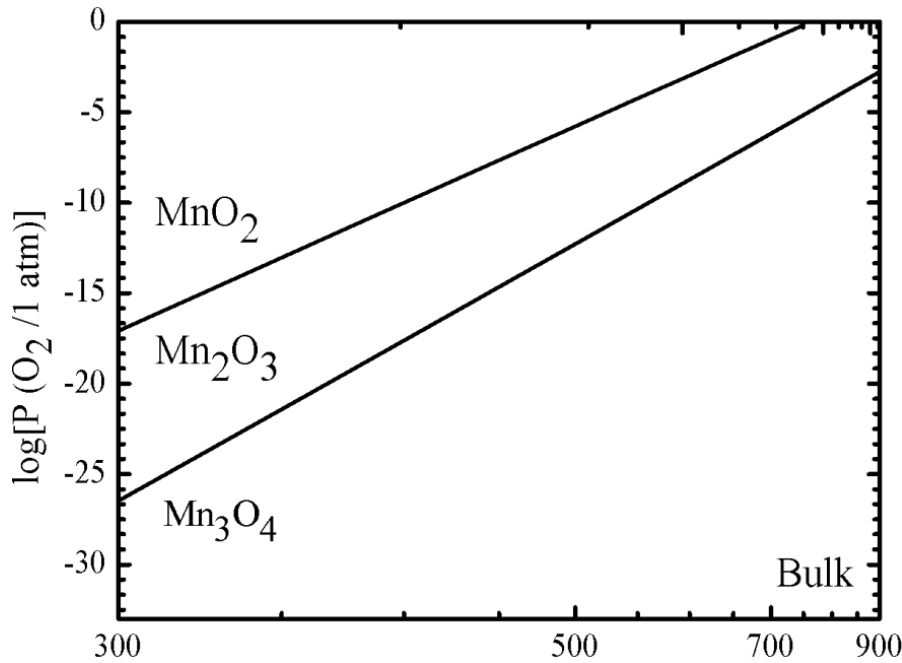


Surface Energy results:

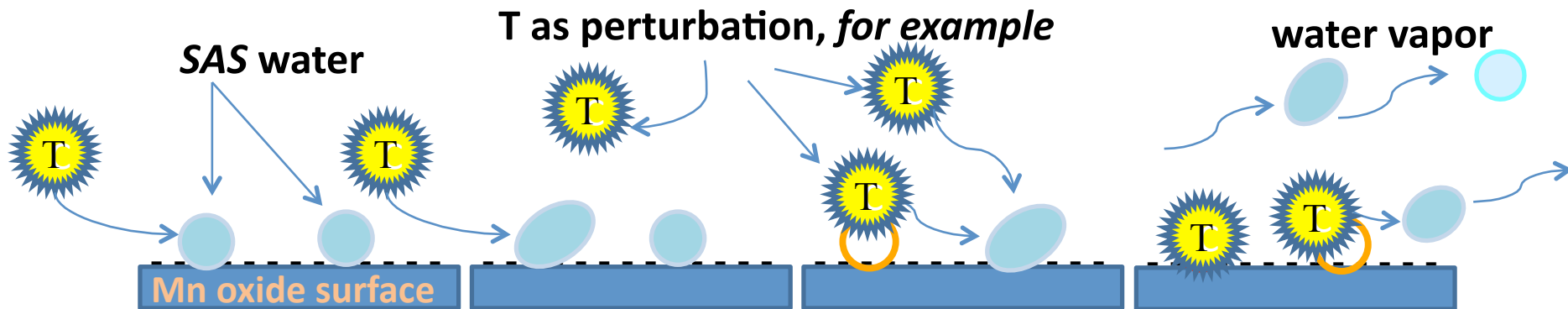


Surface Energy: hydrus < anhydrous

Surface free energy (SFE) shifts favor the nanophase Mn oxides of lower SE. Surface hydration enhances SFE shifts.



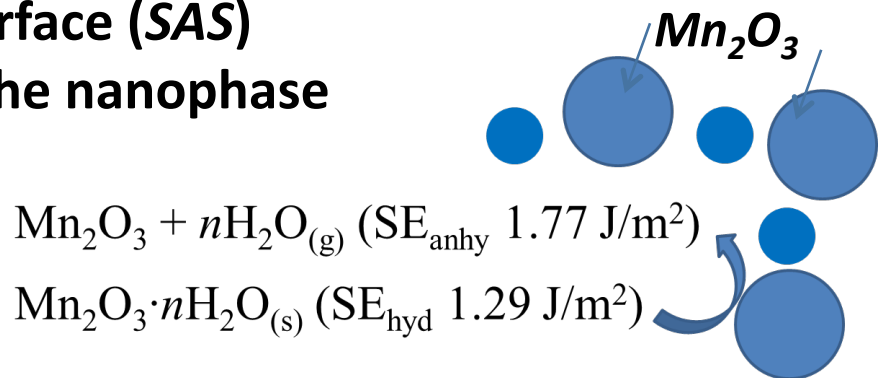
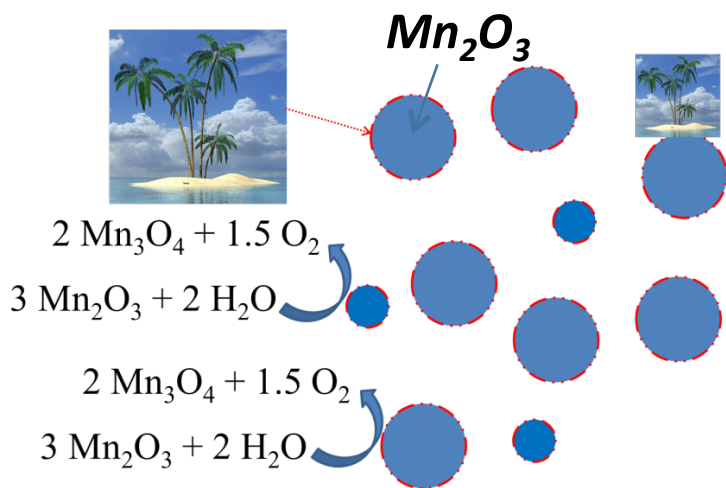
Birkner and Navrotsky (2012) Am. Mineral.



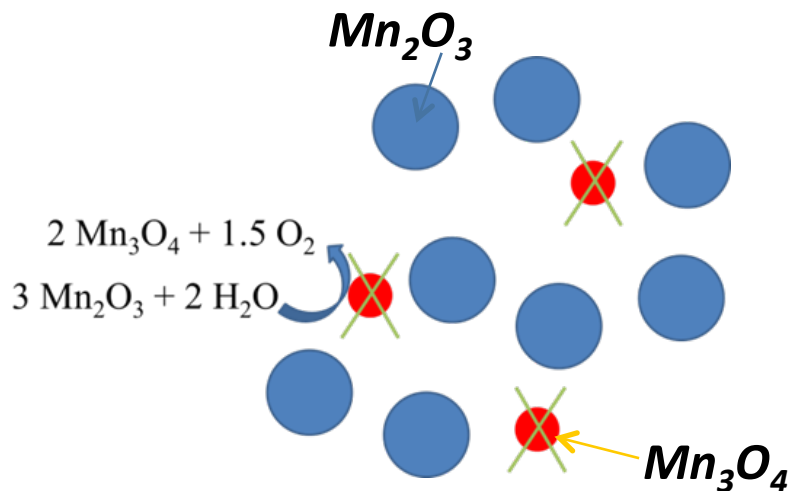
Removal of strongly-associated surface (SAS) water thermodynamically drives the nanophase surface energy (SE) to increase

Why only 15% transformation???
What's the mechanism?!

Mn₃O₄ island formation



&/or



Small particle size mediated transformation

Implications of Redox Shifts

- **Catalysis, hydrogen production, water splitting, batteries, sensors**
- Environmental redox of Fe, Cr, U....
- Biology, origin of life, interpretation of data from Mars
- **THERMODYNAMICS AS WELL AS KINETICS**

The Path Forward

- *Rigorous* - include surface energy as a variable for all phases and calculate equilibria for given particle sizes
- *Practical* – Choose particle size of 10 and 100 nm and add constant free energy terms to each phase (estimating when necessary) and calculate phase diagrams for “small” and “very small” particle systems

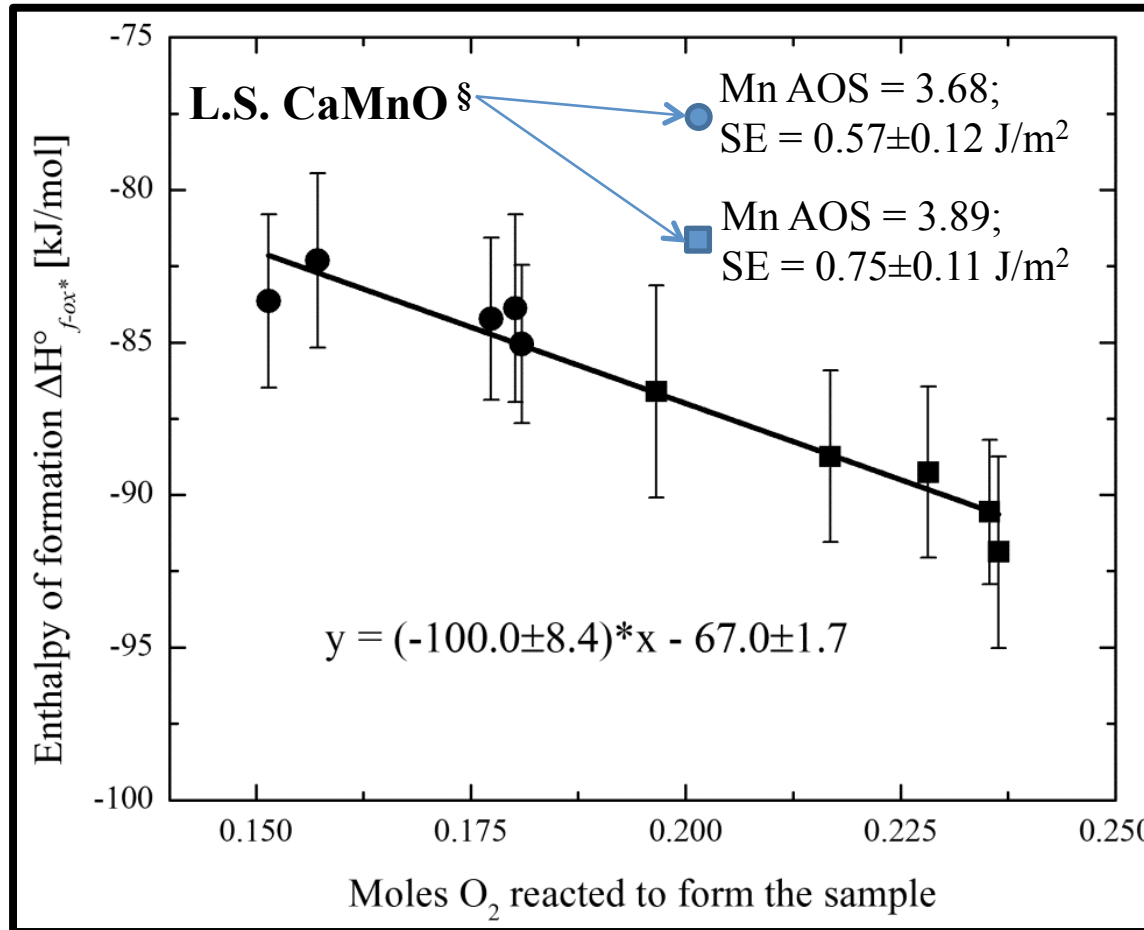
Catalysis, sensors, batteries: some recent studies

- “CoO” catalysts for CO oxidation probably are Co_3O_4 , low surface energy may be important both thermodynamically and catalytically
- SnO_2 a better gas sensor than TiO_2
- “*CaMnO*” catalyst for water splitting, a biomimetic of Photosystem II in photosynthesis
- Li battery materials- nanoscale effects

CaMnO water splitting catalysts

- Nominally $\text{CaMn}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ and $\text{CaMn}_3\text{O}_6 \cdot n\text{H}_2\text{O}$ but actually more oxidized so there is Mn^{3+} and Mn^{4+}
- Nanophase layered birnessite related structure
- Low surface energy

Energetic Basis of Catalytic Activity of Layered Nanophase Calcium Manganese Oxides for Water Oxidation



ΔH_{fox^*} as a function of reacted mols O_2 to form the CaMnO^\S sample.

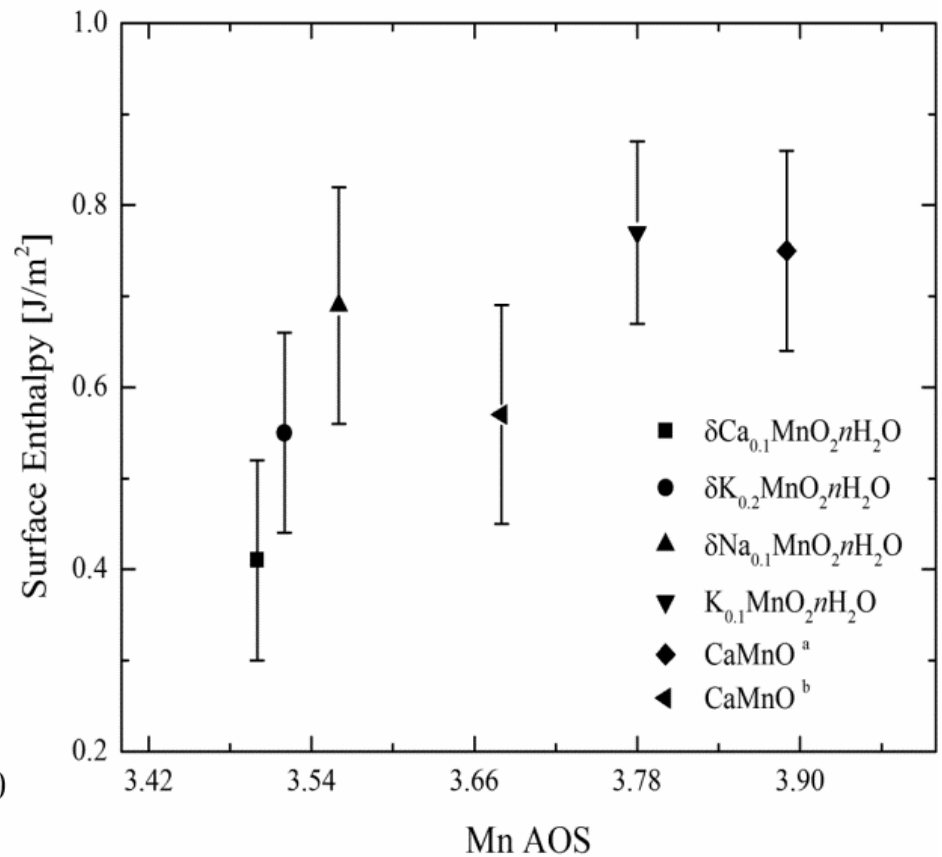
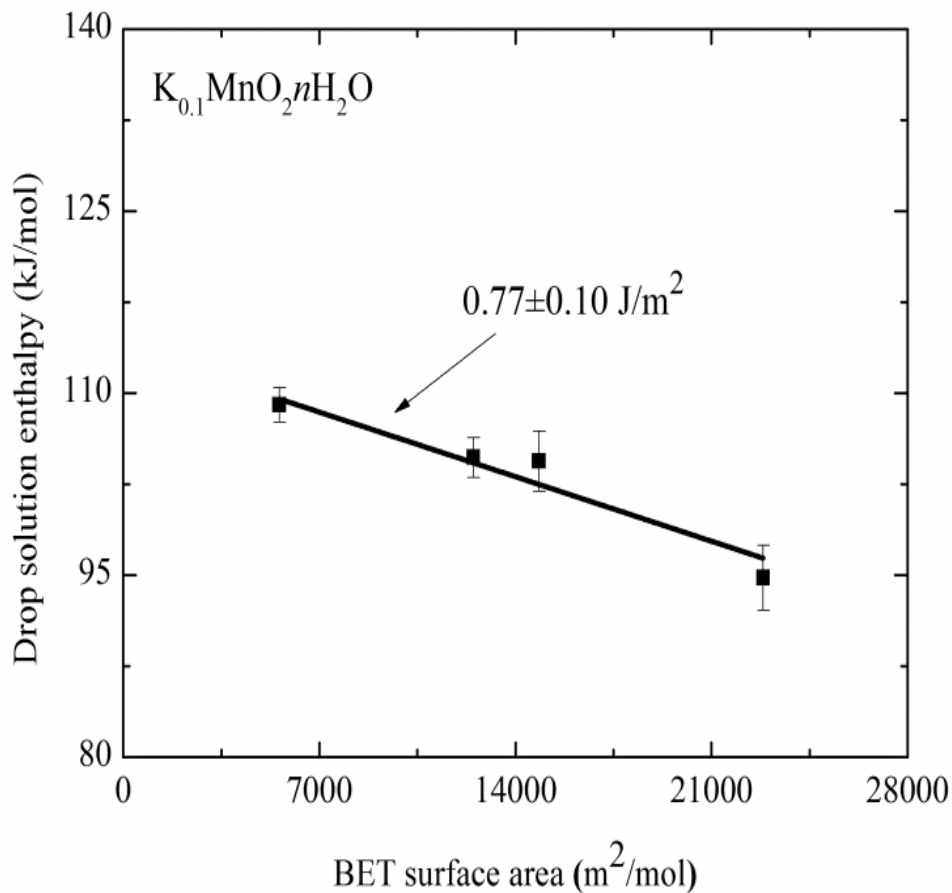
Layered Structure (L. S.)

CaMnO^\S has low surface energy, holds water relatively loosely on its surfaces, and has a variable Mn oxidation state within a single phase.

Internal enthalpy of oxidation of L. S. CaMnO^\S is:

1. Independent of $\text{Mn}^{3+} : \text{Mn}^{4+}$ and $[\text{Ca}^{2+}]/[\text{Mn}]$
2. Much less exothermic than $\text{Mn}_2\text{O}_3/\text{MnO}_2$ redox couple ($\Delta H_{\text{oxidation}} = -168 \text{ kJ/mol}$) O_2

\S CaMnO is a composition notation representative of:
 $m\text{CaO} + [x+y] \cdot \frac{1}{2}\text{Mn}_2\text{O}_3 + [y/4] \cdot \text{O}_2 + n\text{H}_2\text{O} = \text{CaMnO}^\S$



Birnessites all have low surface energies

Left - representative relation of water-corrected enthalpy of drop solution versus surface area, slope of line gives the surface energy. Right - variation of surface energy with manganese average oxidation state (AOS). Birkner and Navrotsky, in preparation.

Battery materials

Redox equilibria and therefore electrochemical potential may depend on particle size. Surface energies?

Recent work on LiCoO_2

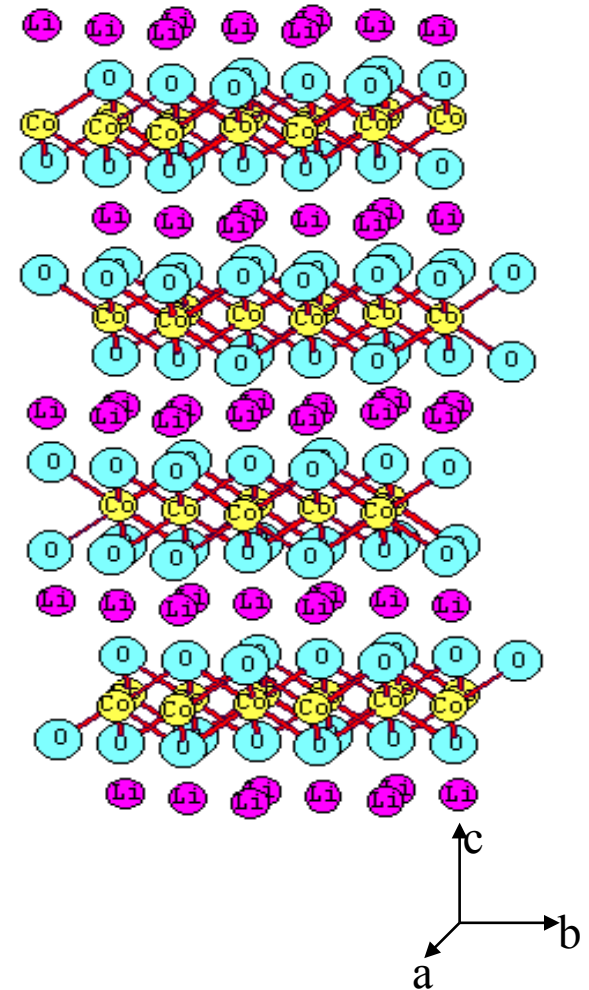
Thermodynamics of other new materials, e.g. triplite-tavorite

LiCoO₂ : Layered rocksalt - derived structure

Hexagonal, R-3m
a = 2.82 Å ; c = 14.08 Å

Cubic close packing of oxide ions – octahedral sites of alternate layers are occupied by Li & Co respectively

LiCoO₂ / Li battery: Li⁺ ions intercalate/
deintercalate



Surface energy

Energy of hydrous surface –

$$2.10 \pm 0.35 \text{ J m}^{-2}$$

Energy of anhydrous surface -

$$2.29 \pm$$

0.35 J m^{-2} almost no stabilization by hydration

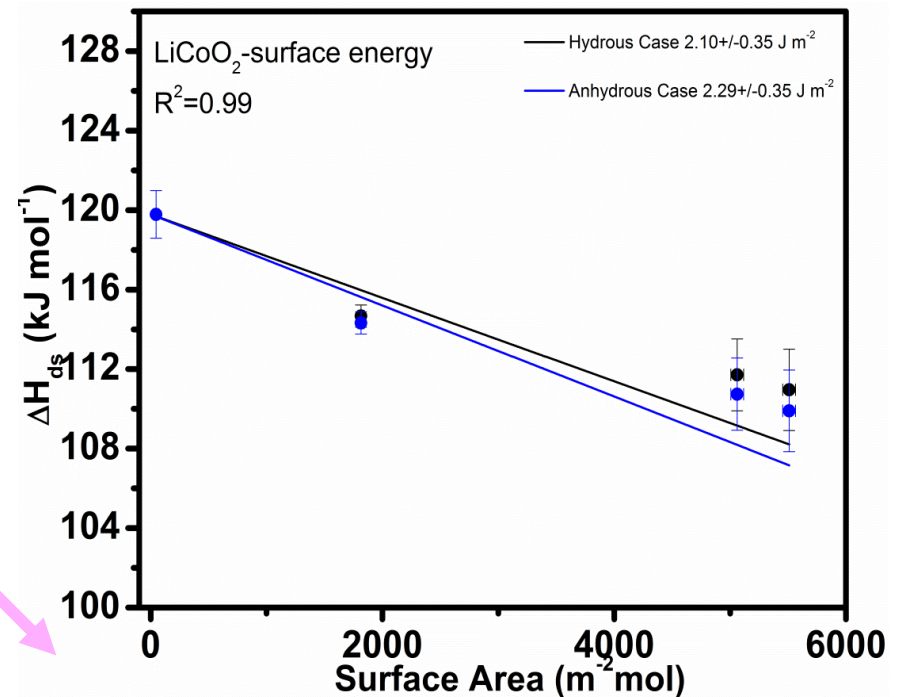
Compare to CoO

Energy of hydrous surface –

$$2.82 \pm 0.20 \text{ J m}^{-2}$$

Energy of anhydrous surface -

$$3.57 \pm 0.30 \text{ J m}^{-2}$$



DFT calculations, Shirley Meng group (2012), give 2.1 J/m² for anhydrous surface, influenced by coordination geometry and spin state of Co³⁺

General Principle ??

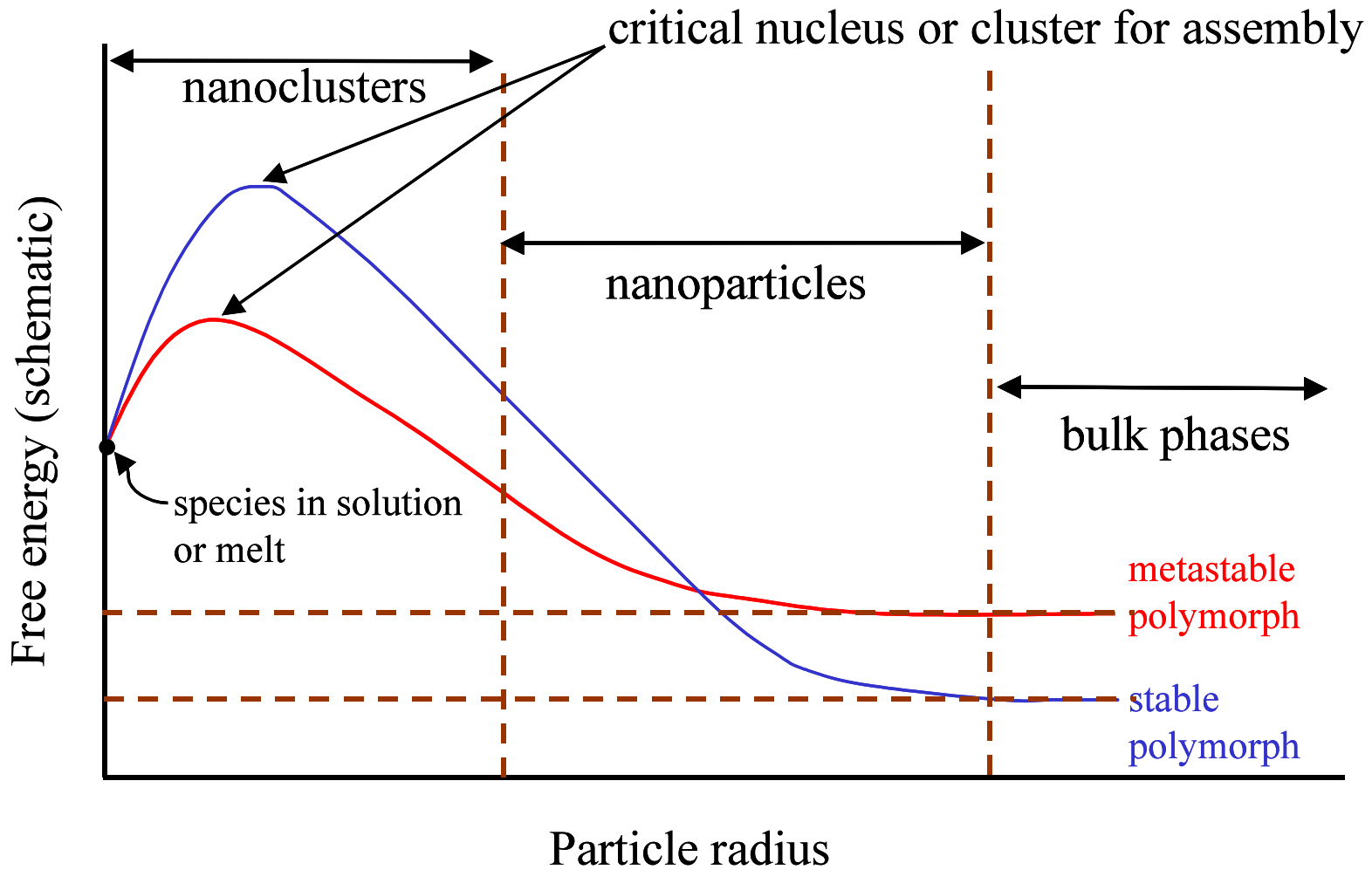
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The best functional and catalytic materials have relatively low surface energies and low affinity for H₂O so that the other species on which they must act can gain access to their surfaces.

Carbonates

- Prenucleation clusters → amorphous carbonates → nanophases → calcite
- Series of downhill steps governed by surface energy, hydration, polymorphism
- Ostwald step rule

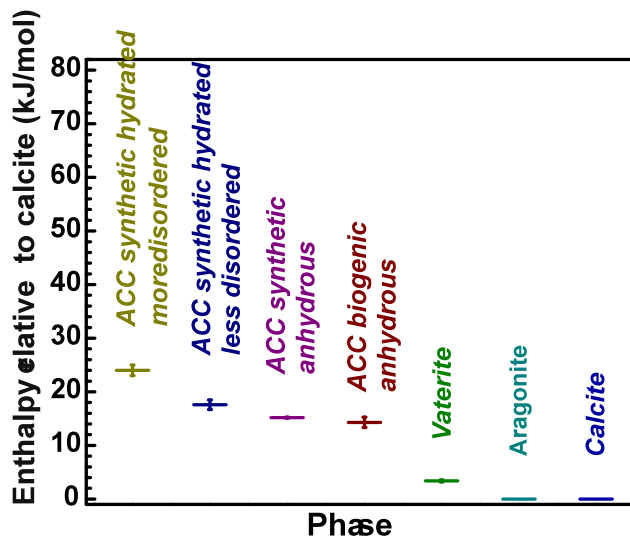
Ostwald Step Rule



Transformation and Crystallization Energetics of Synthetic and Biogenic Amorphous Calcium Carbonate (ACC)

The transformation/crystallization enthalpies were measured using isothermal acid solution calorimetry and differential scanning calorimetry (DSC)

Major findings

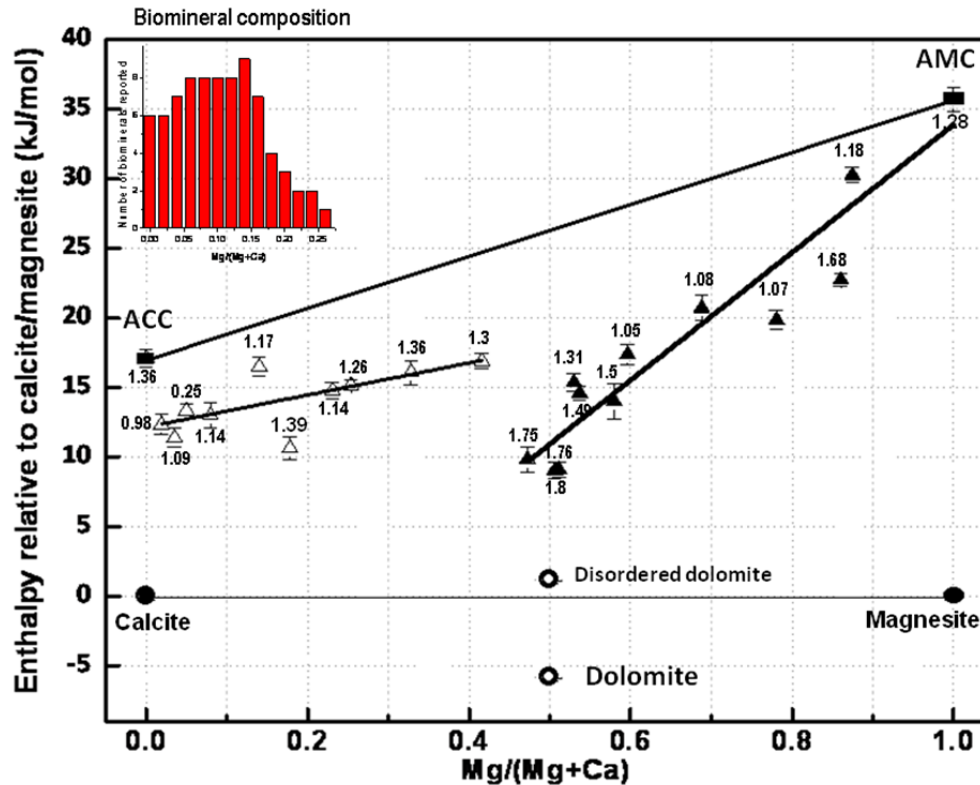


- ACC is a highly metastable phase compared to all crystalline CaCO_3 polymorphs
- Dehydrated synthetic ACC produced by heating is energetically similar to biogenic ACC
- The formation of anhydrous ACC from hydrated ACC is exothermic
- ACC crystallization is energetically downhill through stepwise evolution of series of phases :

More metastable hydrated ACC → Less metastable hydrated ACC ⇒ Anhydrous ACC ~ Biogenic anhydrous ACC ⇒ Vaterite → Aragonite → Calcite

Energetics of Amorphous $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$

AMC is more metastable than ACC but more persistent



Two distinct regions of amorphous $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$ ($0 < x < 1$) phases

Homogeneous single phase ($x < 0.47$) and heterogeneous two phases ($x > 0.47$)

Two distinct amorphous precursors

$x = 0-0.2$ - less metastable single phase is frequently found in biogenic carbonates

$x \sim 0.5$ - least metastable phase could possibly be dolomite precursor

Science is a dog's life!!!

